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TITLE: COMPOSITE CONDUCTIVE POWDER AND CONDUCTIVE FILM

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INVENTOR-INFORMATION:
NAME
HAYASHI, HISAO
YOSHIMARU, KATSUHIKO

ASSIGNEE-INFORMATION:
NAME
MITSUI MINING & SMELTING CO LTD

COUNTRY
N/A

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ABSTRACT:

PURPOSE: To provide composite conductive powder and a conductive film by reducing the content of indium, which causes highest material cost among ITO films, so as to make high transparency comparative with high conductivity even in a coating method.

CONSTITUTION: A conductive film is formed of composite conductive powder obtained by baking a mixture of indium oxide powder containing tin oxide, titanium oxide or zirconium oxide as a dopant with tin oxide powder containing antimony oxide, tantalum oxide or niobium oxide as a dopant.

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CLAIMS

[Claim(s)]

[Claim 1] Compound conductivity powder which calcinates the mixture of the indium oxide system powder which contains at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide as a dopant, and the tin-oxide system powder which contains at least one sort of antimony oxide, tantalum oxide, and niobium oxide as a dopant, and is obtained.

[Claim 2] The indium oxide system powder which contains at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide as a dopant, It is the compound conductivity powder which calcinates mixture with the tin-oxide system powder which contains at least one sort of antimony oxide, tantalum oxide, and niobium oxide as a dopant, and is obtained. The indium oxide in this compound conductivity powder comparatively x %, The dopant of the tin oxide which becomes y % from at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide comparatively comparatively a %, Antimony oxide, the dopant which consists of at least one sort of tantalum oxide and niobium oxide -- comparatively -- b % -- relational-expression: -- $x+y+a+b=100$ $x:a=90:10-99.9:0.1$ $y:b=90:10-99.9:0.1$ $(x+a):(y+B)=3:7-7:3$ Compound conductivity powder characterized by being satisfied.

[Claim 3] The particle size of D90 in particle size distribution is 0.01-5 micrometers, specific surface area is 5-100m²/g, and a volume resistivity is 10⁻⁴-10². Compound conductivity powder according to claim 1 or 2 which is omega-cm.

[Claim 4] Electric conduction film formed using compound conductivity powder according to claim 1, 2, or 3.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the compound conductivity powder and electric conduction film which have high transparency and were excellent in conductivity. It is the thin film which has high conductivity and has light reflex nature to an infrared region about the electric conduction film in more detail with high transparency to a visible region. Especially The transparent electrode of display devices, such as a flat display liquid crystal display component and an electroluminescence display device, Fields, such as infrared (heat ray) reflection of windowpanes, such as fields, such as an internal electrode of a solar battery, an automobile, an aircraft, and a building, Furthermore, it is used for the magnetic-recording medium fields, such as fields, such as CRT as which fields, such as a copying machine-related electrification roller with which electric charge adjustment is demanded, a photoconductor drum, and a toner, and dust antisticking are required, and the Braun tube, an optical disk, FD, and a tape, etc. [0002] Moreover, about compound conductivity powder, also when distributed kneading can be easily carried out into a coating, ink, an emulsion, a polymer, etc., it adds in coatings and it is used as a paint film on the occasion of the use, it is high transparency and excels in conductivity.

[0003]

[Description of the Prior Art] Conventionally, the tin oxide (ATO) which doped antimony as an ingredient of the transparence electric conduction film, the zinc oxide (AZO) which doped aluminum, the indium oxide (ITO) which doped tin are known. Each of these is the semi-conductors of n mold, and especially, since the ITO film has high conductivity compared with the ATO film and the AZO film, and its light transmittance about a visible region is high and pattern NINGU by etching is easy for it, it is widely used in the field of transparence electric conduction film, such as a liquid crystal display component and an electroluminescence display device.

[0004] As the manufacture approach of the ITO film, there are vacuum deposition, a spatter, a spray method, the applying method, etc. Vacuum deposition and a spatter are actually used from the ability of the ITO film of comparatively low resistance to be manufactured with sufficient repeatability. However, the ITO film by vacuum deposition

and the spatter has a problem in a cost rise, mass-production nature, etc. by a membrane formation facility being a large sum, and moreover, since the cost of materials of the ITO itself is high, the ratio of the cost of the electric conduction film occupied to the cost of the whole product is high. Then, development of the transparence electric conduction film by the manufacture process which was excellent in low cost at mass-production nature is desired strongly.

[0005] Moreover, although it is cheap and there are a spray method and the applying method as an approach with sufficient mass-production nature, a spray method has a problem in the homogeneity of membraneous quality and thickness, and repeatability for the spraying pyrolysis in an elevated temperature. Although it is advantageous at points, such as membrane formation area and membrane formation temperature, as compared with other approaches since it is easy pattern formation since the print processes of a coating are used for the applying method, and the yield of ITO which is an expensive ingredient is high The conductivity of 50-100ohms / ** average of the ITO film which the specific surface area of fine particles is very large in order to use a particle, then is easy to be influenced of scaling, and causes the remarkable fall of the carrier electron density in the result table surface layer, therefore is obtained by a spatter etc. is not yet acquired.

[0006] although there are some which were indicated by JP,60-186416,A, JP,63-11519,A, JP,2-120374,A, JP,5-201731,A, JP,5-221639,A, etc. conventionally as conductive powder which forms the transparence electric conduction film which uses indium oxide as a principal component -- any -- In 2O₃ more than 80 mol % -- it contains. Although dopants, such as Sn, are added and improvement in the carrier electron density by the donor is generally measured in order to raise conductivity That the addition of Sn increases with passing (the relative amount of In 2O₃ falling as a result) Since conductivity will fall when a neutral compound defect is formed or carrier electronic mobility falls by grain boundary dispersion and ion impurity scattering, they are a lot of [as mentioned above] In(s) 2O₃. It is made to contain.

[0007]

[Problem(s) to be Solved by the Invention] Even if the purpose of this invention reduces the content of the high indium of especially ingredient cost and it uses it by the applying method also in the ITO film, it is to offer the high conductivity multiple oxide powder and electric conduction film which may reconcile high transparency and high conductivity.

[0008]

[Means for Solving the Problem] Many things are examined about the means which can raise the carrier electron density of a conductive powder front face even if it reduces an indium content in order that this invention person etc. may attain the above-mentioned purpose. The conductive powder of the indium oxide system containing at least one sort of dopants and the conductive powder of the tin-oxide system containing at least one sort of dopants are mixed (with desirable specific compounding ratio within the limits). A header and this invention were completed for the compound conductivity powder which can attain the above-mentioned purpose being obtained by calcinating.

[0009] That is, the compound conductivity powder of this invention is compound conductivity powder which calcinates the mixture of the indium oxide system powder which contains at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide as a dopant, and the tin-oxide system powder which contains at least one sort of antimony oxide, tantalum oxide, and niobium oxide as a dopant, and is obtained.

[0010] moreover, the electric conduction film of this invention -- the compound conductivity powder like the above -- using -- vacuum deposition, a spatter, a spray method, the applying method, etc. -- or it adds in coatings and membranes are formed as a paint film.

[0011] Conductivity is improved rather than the conductive powder of the indium oxide system of the former [powder / of this invention / compound conductivity]. Although it is unknown for details about the mechanism by which such amelioration is attained in the compound conductivity powder of this invention, it is presumed as follows.

[0012] The compound conductivity powder of this invention is what is obtained by calcinating the mixture of the above-mentioned indium oxide system particle powder (for example, ITO particle powder) and tin-oxide system particle powder (for example, ATO particle powder). The dopant in the particle powder of another side carries out minute amount diffusion on the particle front face of one particle powder in the case of this baking (for example, it is thought that Sb^{5+} is permuted by In^{3+} about Sb, and a donor is formed). It is spread from the particle powder of a dopant (for example, respectively Sn and Sb) and another side which exists in the particle front face of these two kinds of each particle powder from the first. A dopant (Dopant A and Dopant B) (for example, Sn and Sb) with both dopants (for example, respectively Sb and Sn) of the minute amount which came comes to exist, and carrier electron density increases. Since conductive powder of a different kind is maintained by the loose contact condition of mixing in the case of this baking, the dopant in the particle powder of another side is not superfluously spread like the time of a consolidation condition, therefore the superfluous concentration of the dopant in each particle powder front face is controlled by the particle front face of one particle powder, and there is no fall of the carrier electron mobility by dispersion of an ionization impurity. Furthermore, since it is calcinated, the crystallinity of particle powder becomes good, and it is thought that grain boundary dispersion of a carrier electron decreased. Moreover, both dopant A and dopant B are presumed to be what raises carrier electron density and carrier mobility in a certain form.

[0013] In the compound conductivity powder of this invention, although at least one sort of antimony oxide, tantalum oxide, and niobium oxide is used as a dopant of tin-oxide system powder, using at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide as a dopant of indium oxide system powder, this selection is the result of inquiring in consideration of the valence and ionic radius of ion of each metal.

[0014] Moreover, when adding in coatings and using the compound conductivity powder of this invention as a paint film, high transparency is required, it is desirable that it is so below the half-wave length of the light (400-800nm) as a diameter of a primary particle of particle powder, and it is still more desirable that the dispersibility in the inside of resin is raised.

[0015] The indium oxide system particle conductivity powder and tin-oxide system particle conductivity powder which are used in order to obtain the compound conductivity powder of this invention are as follows, respectively. For indium oxide system powder, it consists of at least one sort of dopants chosen from the group which consists of 0.1 - 10% of the weight of Sn, tetravalent Ti, and tetravalent Zr preferably on the weight criteria of indium oxide and this indium oxide, the particle size of D90 in particle size distribution is 0.01-5 micrometers preferably, specific surface area is 5-100m² / g preferably, and a volume resistivity is 10⁻³-10³ preferably. It is omega-cm. When the content of a dopant is less than 0.1 % of the weight, the addition effectiveness is insufficient, and since the addition effectiveness may be reaching the ceiling and may have a bad influence on conductivity conversely even if it adds exceeding 10 % of the weight, it is not desirable.

[0016] Moreover, for tin-oxide system powder, it consists of at least one sort of dopants chosen from the group which consists of 0.1 - 10% of the weight of Sb, pentavalent Nb, and pentavalent Ta preferably on the weight criteria of diacid-ized tin and this diacid-ized tin, the particle size of D90 in particle size distribution is 0.01-5 micrometers preferably, specific surface area is 5-100m² / g preferably, and a volume resistivity is 10⁻³-10³ preferably. It is omega-cm. When the content of a dopant is less than 0.1 % of the weight, the addition effectiveness is insufficient, and since the addition effectiveness may be reaching the ceiling and may have a bad influence on conductivity conversely even if it adds exceeding 10 % of the weight, it is not desirable.

[0017] In this specification, the particle size of D10, D50, and D90 in particle size distribution means the particle size of the fines of the part which accumulates the amount of fines from the one where particle size is smaller, and becomes 10%, 50%, and 90%, respectively.

[0018] The tin-oxide system powder used in order to obtain the compound conductivity powder of this invention is obtained by the following manufacture approach. On the weight criteria of this diacid-ized tin that contained stannic salt by the concentration of 0.5-10 mol / l preferably, and converted this stannic salt into diacid-ized tin, preferably 0.1 - 10% of the weight of Sb, The alkaline solution or acidic solution containing at least one sort of compounds chosen from the group which consists of a pentavalent compound of Sb, Nb, and Ta of the amount used as Nb or Ta, Coincidence is separately followed, respectively in the neutralization solution which neutralizes Sb, Nb, or Ta compound content stannic-salt solution. this -- a reaction vessel It introduces into (for example, the bottom of the tank of a reaction vessel), and high-speed stirring of both the solutions is immediately carried out together after installation. In an instant Homogeneity mixing of both solutions, The coprecipitation Mr. object which promotes detailed distribution of homogeneity karyogenesis and a coprecipitation Mr. object, maintains the inside of a reaction vessel to a fixed pH value predetermined by within the limits of pH 2-12 in this case, and has detailed and sharp particle size distribution is deposited continuously. By making the solution after a reaction, and a reaction coprecipitation Mr. object into a slurry, it discharges continuously from a reaction vessel (for example, reaction-vessel upper part), solid-liquid-separation processing of the slurry is carried out, coprecipitation

Mr. objects are collected, it dries, and after that, among air or inactive or a weak reducing atmosphere, it calcinates at 300-800 degrees C, and conductivity is given.

[0019] In the above-mentioned manufacture approach, any of an acidic solution or an alkaline solution are sufficient as Sb, Nb, or Ta compound content stannic-salt solution to be used, and it is not limited especially as the stannic salt, Sb compound, Nb compound, and a Ta compound. for example, when Sb, Nb, or Ta compound content stannic-salt solution is an acidic solution Tin chloride, sulfuric-acid tin, nitric-acid tin, acetic-acid tin, etc. can be used as stannic salt. As Sb compound, Nb compound, or a Ta compound, a chloride, a fluoride, a sulfate, A halogenide etc. can be used, it can add in a stannic-salt solution as a solution, for example, a water solution, and an alcoholic solution, and those Sb compounds, Nb compound, or Ta compound can be used as Sb, Nb, or a Ta compound content stannic-salt solution. moreover, when Sb, Nb, or Ta compound content stannic-salt solution is an alkaline solution Stannic-acid sodium, a stannic-acid potassium, etc. can be used as stannic salt. As Sb compound, Nb compound, or a Ta compound, a chloride, a fluoride, a sulfate, A halogenide, $K_2 NbOF_5$, $H_2 O$, etc. can be used. It can add in a stannic-salt solution as a solution, for example, a water solution, and an alcoholic solution, and those Sb compounds, Nb compound, or Ta compound can be used as Sb, Nb, or a Ta compound content stannic-salt solution.

[0020] As a neutralization solution which neutralizes above Sb, Nb, or Ta compound content stannic-salt solution, when Sb, Nb, or Ta compound content stannic-salt solution is an acidic solution, water solutions, such as a sodium hydroxide, a potassium hydroxide, ammonia, and a sodium carbonate, can be used, and when Sb, Nb, or Ta compound content stannic-salt solution is an alkaline solution, thin water solutions, such as a hydrochloric acid, a sulfuric acid, a nitric acid, and an acetic acid, can be used. As for the concentration of a neutralization solution, it is desirable that it is 0.5 to 5 times the concentration of Sb, Nb, or Ta compound content stannic-salt solution. If dilution past ** and the amount of waste fluid increase [the concentration of a neutralization solution] in vain, costs increase to waste fluid processing and the concentration of a neutralization solution is too thick conversely, since it is difficult to maintain a pH value uniformly, and it originates in that, and particle size distribution tend to become broadcloth and it becomes easy to generate problems, such as adhesion of a scale in a pH electrode etc., it is not desirable.

[0021] Solid-liquid-separation processing (filtration) is carried out, the slurry obtained as mentioned above is washed, coprecipitation Mr. objects are collected, it dries and 300-800 degrees C is preferably calcinated at 450-700 degrees C among inactive or a weak reducing atmosphere among air after that. When burning temperature is less than 300 degrees C, the donor formation by the dopant is not enough, and since diacid-ized tin is not fully crystallized, there is an inclination for conductivity to become inadequate. Moreover, in exceeding 800 degrees C, it sinters and a big and rough particle arises, and transparency is hard to be acquired, when it adds in coatings and covers as a paint film.

[0022] The firing environments adopted by the above-mentioned manufacture approach is H_2 to these inert gas also in the inside of air, or inert gas ambient atmospheres, such as N_2 , and helium, Ne, Ar, Kr. Or less than [20vol%] and the weak reducing atmosphere

preferably added by 0.1 - 5vol% concentration are sufficient in reducibility gas, such as CO. When the reducing atmosphere to which the concentration of the reducibility gas added in inert gas exceeds 20vol(s)% was used, and reduction progresses further and it takes out from the diacid-ized tin of stoichiometry in air, it oxidizes rapidly, and occasionally ignite and it may sinter. Moreover, generation diacid-ized tin becomes deep blue or deep blackish brown by advance of reduction, and it is not desirable in respect of a color tone.

[0023] Indium oxide system particle conductivity powder can also be manufactured by the manufacture approach of the above-mentioned tin-oxide system particle conductivity powder, and the same approach.

[0024] The compound conductivity powder of this invention can be obtained by the following manufacture approach. first, the above-mentioned tin-oxide system particle conductivity powder and indium oxide system particle conductivity powder -- a weight ratio -- desirable -- 3:7-7:3 -- it mixes before and behind 1:1 most preferably. Mixing of particle powder does not interfere at all, whether it uses well-known grinders, such as well-known dry-blending machines, such as a mortar, a kneader, and a blender, a ball mill, a pin mill, and a sand mill, or it makes it the shape of a slurry and a ball mill, a high-speed agitator, a paint shaker, a bead mill, etc. carry out wet-grinding mixing.

[0025] In mixing by the shape of a slurry, after drying, 300-800 degrees C of mixed particle powder are preferably calcinated at 450-700 degrees C among air or inactive or a weak reducing atmosphere. When burning temperature is less than 300 degrees C, the diffusion to the different-species powder of a dopant is not enough, and since it does not fully crystallize, conductivity is inadequate. Moreover, in exceeding 800 degrees C, it sinters and a big and rough particle arises, and transparency is not acquired, when it adds in coatings and covers as a paint film.

[0026] The firing environments used by the above-mentioned manufacture approach is H₂ to these inert gas also in the inside of air, or inert gas ambient atmospheres, such as N₂, and helium, Ne, Ar, Kr. Or less than [20vol%] and the weak reducing atmosphere preferably added by 0.1 - 5vol% concentration are sufficient in reducibility gas, such as CO. When the reducing atmosphere to which the concentration of the reducibility gas added in inert gas exceeds 20vol(s)% was used, and reduction progresses further and it takes out from diacid-ized tin and indium oxide of stoichiometry in air, it oxidizes rapidly, and occasionally ignite and it may sinter. Moreover, generation powder becomes the ashes black which wore blueness by advance of reduction, also in respect of a color tone, indium oxide forms the InSn₄ grade of a low-melt point point, it condenses and the powder obtained makes it big and rough further preferably.

[0027] The compound conductivity powder of this invention so that clearly [the above explanation list] from the after-mentioned example x % of rates of the indium oxide in this compound conductivity powder and the tin oxide comparatively y %, The dopant (henceforth Dopant A) which consists of at least one sort of the tin oxide, titanium oxide, and a zirconium dioxide comparatively a %, The dopant which consists of at least one sort of antimony oxide, tantalum oxide, and niobium oxide The thing of (calling it Dopant B hereafter) for which b % satisfies relational-expression: $x+y+a+b=100$

$x:a=90:10-99.9:0.1$ $y:b=90:10-99.9:0.1$ $(x+a):(y+B)=3:7-7:3$ comparatively is desirable.
[0028] In the compound conductivity powder of this invention, the particle size of D90 in particle size distribution is 0.01-5 micrometers, specific surface area is 5-100m² / g, and a volume resistivity is 10⁻⁴-10². It is desirable that it is omega-cm. Since the particle size of D90 in particle size distribution is less than 0.01 micrometers, or the inclination which also sinters low-temperature baking when specific surface area exceeds 100m² / g becomes high and a big and rough particle arises, it is not desirable.

JAPANESE [JP,07-335031,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF
THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE WRITTEN
AMENDMENT

[Translation done.]